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New proton-conductive membranes for fuel cells based on hybrid composites

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Abstract

New hybrid organic-inorganic composites based on sulfur-containing styrene copolymers and allyl glycidyl ether and tetraethoxysilane were obtained by a sol-gel synthesis method. The membranes created on the basis of composites have proton-conductive properties and are characterized by a higher heat-exchange capacity compared with commercial membranes as Nafion and MF-4 SK, enabling to consider them as perspective membrane materials for fuel cells.

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Keywords: copolymers; sol-gel synthesis; hybrid organic-inorganic composites; specific conductivity

1. Introduction

In present days the problem of a global energy crisis related with the emission of a huge amount of toxic wastes as a result of energy resources traditional using aggravated in industrialized countries. It affects negatively the environment and causes irreversible climatic changes. The most urgent problem is searching for an alternative way of power production. One of the solutions of this problem is the development of fuel cells based on a polymeric proton-conductive membrane [1].

According to the analysis of studies on polymeric proton-conductive electrolytic membranes developing there are three groups of polymeric systems suitable for the efficient industrial application [2]:

- perfluorinated sulfur-containing polymers;
- condensation polymeric systems;

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- hybrid polymeric systems (hydrogels and composites).

In industrial scale, membranes based on perfluorinated sulfur-containing polymers are generally used. They are high tech and characterized by high performance values, but they can only be used at temperatures below 90 ºC and, the most important thing is the high cost, because of their production complexity. For example, Nafion membranes consist of a tetrafluorethylene copolymer and a perfluorinated sulfur-containing monomer [3]. Its producing process involves at least five independent technological stages.

Proton-conductive membranes based on condensation systems are, as a rule, formed on the basis of aromatic or heterocyclic high-molecular compounds, for example, based on polybenzimidazole, doped by the phosphoric acid. The advantage of such membranes is a high proton conductivity, considerable heat resistance (up to 600 °C), tolerance to CO and CO_2 impurities, low permeability for different types of fuel, including methanol, high mechanical strength [4]. However membranes based on those polymers are produced now as a pilot project because of the lack of commercial processes of the initial monomers production.

A new promising type of proton-conductive membranes is hybrid composite membranes formed by the method of sol-gel synthesis based on organic polymers and organic-silicon precursors [5]. The introduction of an organic-silicon framework in a polymeric matrix enables to improve significantly mechanical properties and thermal stability of the proton-conductive membranes [6]. An organic component, as a rule, contains functional groups providing a proton transport. The advantage of hybrid composite membranes is the possibility of their obtaining based on organic and hetero-organic synthesis products, which are simple in production technology and cheaper in cost than traditional ones. For example, for synthesis of such membranes styrene copolymer (St) and unsaturated epoxides can be used as an organic polymeric component and a tetraethoxysilane (TEOS) is used as the organic-silicon component.

The purpose of this work was to obtain hybrid organic-inorganic composite materials based on modified St and allyl glycidyl ether (AGE) copolymers using TEOS as an organic-silicon precursor by sol-gel synthesis method, and to study the main characteristics of polymeric membranes obtained on their basis.

2. Experimental

St and AGE copolymers were obtained by a suspension free radical copolymerization method according to [7]. To provide a proton conductivity, copolymers were exposed to preliminary sulfonating by the concentrated sulfuric acid (ρ = 1,825 g/cm^3) in a benzene or toluene solution at the temperature of 60 to 90º C for 1-12 hours. The methods of turbidimetric titration, element analysis (C, H, S weight content), NMR ^{13}C spectroscopy were used to determine the composition and structure of the obtained products. The formation of hybrid composites based on sulfonated copolymers was carried out similarly by sol-gel synthesis method [8]. The composites' structure was established according to the element analysis (S, N, Si weight content) and infrared spectroscopy. The research of the synthesized samples surface structure was conducted by the scanning electron microscopy method. The impedance spectroscopy method was used to characterize the membranes proton conductivity.

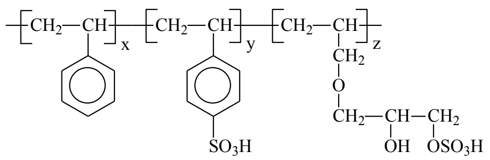
3. Methods

Turbidimetric titration was carried out at the temperature of 25º C, the initial copolymers solution concentration in cyclohexanone was 0,96 g/100 ml, isopropanol was used as a precipitator. The optical density of solutions was determined by photoelectrocolorimeter KFO-1. The element analysis of copolymers and composites was carried out by «Thermo Finnigan Flash EA 1112 Series» gas analyzer. Infra-red spectrums of composites were obtained in KBr tablets and in a microlayer using Specord IR-75 spectrometer, and Bruker IFS-25 spectrometer. NMR ^{13}C spectrums of copolymers were registered on VXR– 500S spectrometer “Varian” (with 125,5 MHz operating frequency) with a noise isolation from protons and with a 2,5 sec relaxation delay. The impulse was 90^o. Solvents were DMSO–d_6 and acetone–d_6. Chrome tris-acetylacetonate (0,02 mol/l) was used as a relaxant. The examination of a surface structure of synthesized samples was conducted by the scanning electronic microscopy method using “Philips-525-M apparatus”. Films electroconductivity was measured by a complex impedance technique in isothermal mode in 500000-5000 Hz frequency range using «Z-500PX» impedancemeter (Elins, Russia).

4. Results and discussion

Sulfonated copolymers St and AGE are powdery substances from cream to dark brown color, having a high solubility in benzene and acetone. The degree of copolymers sulfonation was 12 to 95% mol according to the element analysis.

The main active centers for the sulfonation reaction are a reactive AGE oxirane ring and St aromatic fragments. NMR ^{13}C spectroscopy data are evidence of the process both on aromatic ring, and on epoxy group with the formation of sulfur-aromatic, sulphate and hydroxyl groups in the structure of copolymers



(1)

where $x = 2 \div 72$; $y = 3 \div 43$; $z = 1$.

In spectrums of NMR ^{13}C of sulfonated copolymers there is a signal in the 154-155 ppm field, which corresponds to a chemical shift of a carbon atom of the aromatic ring bound to a sulfur atom. Simultaneously in spectrums signals in the 65-72 ppm field appear, typical for sulphate and hydroxyl groups as a part of AGE links.

A further formation of hybrid composites represents a process of a hydrolytic condensation of the organic-silicone precursor (TEOS) and St-AGE copolymers and results in the formation of a three-dimensional silsesquioxane structure according to the scheme:

$$Si(OC_2H_5)_4 \quad + \quad 2\ H_2O \longrightarrow 1/n(SiO_2)n \quad + \quad 4\ C_2H_5OH \qquad (2)$$

The obtained composites represent powdery products from a light gray to a brown color, consisting of irregular shaped particles with a typical size from 60 to 100, 200 microns (Fig. 1). In IR spectrums of samples there are absorption bands in the 1000-1200 cm^{-1} field characterizing siloxane bond valent fluctuations and also in the 780-830 cm^{-1} field which can be referred to Si-O-C bond valent fluctuations.

The composites retention of homogeneity and mass after processing by high-boiling organic solvents (xylene, dimethylsulfoxide) and mineral acid water solutions (5 mol/l HCl, 5 mol/l H_2SO_4) enables to conclude that these materials, most likely, represent semi-interpenetrating lattices [9].

Based on the obtained hybrid composite materials durable elastic membranes having a high thermal and chemical stability (thermal-oxidative stability temperature was 220 °C) were created. The membranes proton conductivity was measured at 30, 40, 50, 60 °C temperatures and 75% relative humidity. Measurement results are given in table 1.

The analysis and processing of impedance hodographs obtained for hybrid membranes showed that their average specific conductivity was about $1{,}46 \cdot 10^{-3}$ S/cm. With temperature increasing their proton conductivity also increases.

The main characteristics of the obtained membranes compared to the most widespread commercial membranes like Nafion (for example, Nafion 212) and MF-4 SK-1 are shown in table 2.

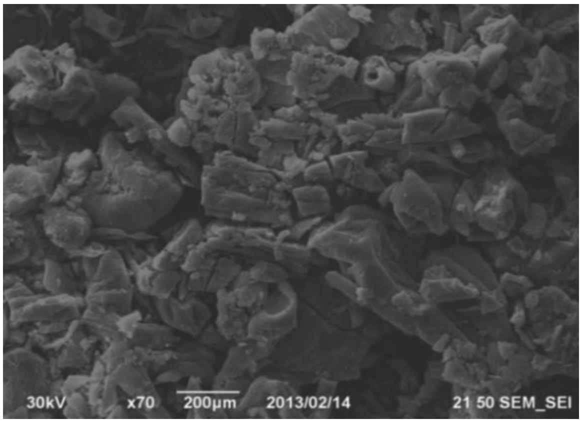


Fig. 1. Electronic microphotography of a composite surface.

Table 1. Measurement results of a hybrid membrane ionic conductivity (S 17,13% mass.).

№	t, °C	$(1/T)\cdot10^3$, K^{-1}	S, cm^2	d, cm	R, Ohm	σ, S/cm	lnσ	E_A, kJ/mol
1	30	3,30	0,139	0,014	227,50	$4,4\cdot10^{-4}$	-7,72	51,11
2	40	3,19	0,139	0,014	97,50	$2,0\cdot10^{-3}$	-6,88	
3	50	3,10	0,139	0,014	62,50	$1,6\cdot10^{-3}$	-6,43	
4	60	3,00	0,139	0,014	36,00	$2,8\cdot10^{-3}$	-5,88	

Table 2. Characteristics of proton-conductive composite membranes.

Name of characteristic	Value of characteristic		
	Nafion 212 membrane	MF-4 CK-1 membrane	Hybrid membranes
Specific conductivity, S/cm	$1,8\cdot10^{-2}$	$1,4\cdot10^{-2}$	$2\cdot10^{-3}$
Activation energy, kJ/mol	17,04	29,9	49,6-51,1
Exchange capacity, mg-eq/g	0,95-1,01	0,90-1,15	1,84-2,70
Modulus of elasticity, MPa	160,0	132,0	15,6

The comparison of the specified parameters shows that the samples of commercial membranes have higher values of the specific conductivity, smaller values of the activation energy and better mechanical properties. However hybrid membranes show a higher exchange capacity compared to commercial membranes (1,84-2,70 and 0,95-1,01 mg-eq/g, respectively) providing the opportunity to consider them as perspective membrane materials for fuel cells.

5. Conclusion

Thus, in the course of the conducted investigations:

- hybrid composite materials with a high elasticity, thermal and chemical resistance and proton conductivity of $1,46\cdot10^{-3}$ S/cm were obtained by the method of hydrolytic condensation of a tetraethoxysilane and sulfonated copolymers of styrene and allyl glycidyl ether;
- a high exchange capacity of the obtained composite membranes compared to commercial membranes as Nafion and MF-4 CK (1,84-2,70 and 0,95-1,01 mg eq/g, respectively) enables to consider them as promising membrane materials for fuel cells.

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References

[1] S.S. Ivanchev, S.V. Myakin, Polimernye membrany dlya toplivnyh elementov: poluchenie, modifitsirovanie, struktura, svoistva, Uspehi himii. 79 (2010) 117-134..

[2] Y.A. Dobrovolsky, E.V. Volkov, A.V. Pisareva, Y.A. Fedotov, D.Y. Lihachev, A.L. Rusanov, Protonoobmennye membrany dlya vodorodno-vozdushnyh toplivnyh elementov, Ros. him. zhurnal. L (2006) 95-104.

[3] Pat. 3282875, USA, 1966.

[4] J.A. Asensio, S. Borrós, P. Gómez-Romero, Proton-conducting polymers based on benzimidazoles and sulfonated benzimidazoles, J. Polym. Sci. Polym. Chem. 40 (2002) 3703-3710.

[5] M. Kato, S. Katayama, W. Sakamoto, T. Yogo, Synthesis of organosiloxane-based inorganic/organic hybrid membranes with chemically bound phosphonic acid for proton-conductors, Electrochim. Acta. 52 (2007) 5924-5931.

[6] P.L. Antonucci, A.S. Arico, P. Creti, E. Ramunni, V. Antonucci, Investigation of a direct methanol fuel cell based on a composite Nafion-silica electrolyte for high temperature operation, Solid State Ionics. 125 (1999) 431-437.

[7] M.A. Chernigovskaya, T.V. Raskulova Radical copolymerization of styrene and allyl glycidyl ether, European Science and Technology: 7th International scientific conference. Munich 2014. Vol. II. 443-448.

[8] O.V. Lebedeva, Y.N. Pozhidaev, E.I. Sipkina, A.N. Chesnokova, N.A. Ivanov, T.V. Raskulova, M.A. Pokrovskaya, Sintez i svoistva sopolimerov i kompozitov na osnove vinilglicidilovogo efira etilenglikolya i vinilhlorida, Plasticheskie massy. 9 (2013) 35-39.

[9] M.G. Voronkov, N.N. Vlasova, Yu.N. Pozhidaev, Organosilicon IonExchange and Complexing Adsorbents, Appl. Organomet. Chem. 14 (2000) 287-313.